# Intensive Biogeochemical Characterization of Sediment Core Provides Unique Insights on Natural Source Zone Depletion

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**Background/Objectives.** Our collective understanding of subsurface natural attenuation of petroleum hydrocarbon (PHC) non-aqueous phase liquids (NAPL), more specifically referred to as natural source zone depletion (NSZD), continues to evolve from research to practice. Microbial sulfate reduction and/or methanogenesis most often drive natural degradation of PHC NAPL, at least beyond initial stages. Biodegradation reactions involving electron acceptors oxygen, nitrate, manganese ($Mn^{III}$ and $Mn^{IV}$), and iron ($Fe^{III}$) are considered important but secondary. The role of amorphous and crystalline Fe and Mn is recognized as potentially important in NSZD, but limited characterization resources are typically focused on the groundwater and soil gas. Consequently, there is a gap in knowledge on the relative importance of Fe and Mn compared to other redox reactants and how biogeochemical characterization can materially contribute to NSZD assessment and demonstration. Here, we present a case study where intensive biogeochemical characterization of sediment core samples was uniquely integrated into a multi-faceted NSZD assessment.

The former fuels facility had been in operation over 80 years, and during that time various grades of jet fuel were inadvertently released into the soil and groundwater resulting in a 20-acre NAPL plume. A series of characterizations and remedial actions over 30 years reduced PHC impacts, but the core of NAPL impacts has survived and this may be due in part to the fact that the surviving NAPL is relatively deeply seated in saturated sands. Prior to restarting active remediation, the natural, existing geochemical and biodegradation conditions were assessed to (1) document the site's capacity for natural degradation of jet fuel NAPL, and (2) provide baseline conditions to guide the selection and implementation of a final time-efficient remedy. The selected remedy includes expanded networks of soil vapor extraction, NAPL removal, and air sparging, but complete NAPL removal is unlikely, and closure will require defensible data to demonstrate NSZD.

**Approach/Activities.** The NSZD assessment included a unique mix of geochemical and mineralogical testing of subsurface sediment samples collected from nine locations and three depth intervals using Geoprobe Systems® dual-tube sampling system and special techniques to reduce oxygen and ambient microbial exposure. Redox sensitive aliquots and dried and split aliquots were prepared for use with 14 different characterization tests. A major thrust was elemental, petrographic, and mineralogical quantification of redox active Fe, Mn, and sulfur (S) concentrations, forms, and mineral morphologies from sand size to 0.3 micrometer and then to elemental level.

**Results/Lessons Learned.** The intensive biogeochemical characterization has borne significant insights and confirmed the diagnostic value of Fe, Mn, and S in discerning details of historical/recent NAPL and dissolved-phase biodegradation. Use of strong and weak acid extractions of aliquots and tests documenting the occurrence and morphology of iron sulfides and magnetite proved instrumental in identifying advanced NAPL degradation in two areas, a key line of evidence for NSZD. An alternative electron acceptor capacity model was developed and applied to generate a range of input into subsequent NSZD assessment.